THROWING POWER IN THE $CuSO_4 \cdot 5H_2O$-H_2SO_4-H_2O SYSTEM

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A number of papers have been devoted to the throwing power of copper-sulfate electrolytes [1-8]. None of these, however, has covered the whole range of possible concentrations of copper sulfate and sulfuric acid. The complete picture of the relation between the throwing power of the electrolyte and the concentration of the components cannot even be obtained by amalgamating the results of different authors, since the latter used measuring cells of different constructions and numerically-incompatible methods of determining the uniformity of current distribution.

METHOD

In order to estimate the throwing powers of the electrolytes we used the index $R_i = a_{cp}/\rho$ [9], which included no geometric parameters of the measuring cell and constituted a function of the electrolyte properties only. The value of R_i was measured directly by means of a slotted cell with a sectional cathode [10]. The essence of the method lay in using the relationship between the ratio of the currents flowing through the two sections of the cathode and the value of the index R_i. For the majority of the measurements we used a cell with cathode sections 2.45 and 7.55 cm long. In electrolytes with a small concentration of copper sulfate, where R_i was much greater than unity, a sectional cathode with sections 4.38 and 5.62. cm long was used. This ensured the greatest accuracy of measurements in the range R_i = 10 to 50 cm. Calculation of the calibration curve for this case (see Appendix), as in an earlier case [10], was carried out numerically, assuming that linear polarization occurred at the cathode. For cathode sections 4.38 and 5.62 cm long the corresponding currents were identical for R_i = 20 cm. The calibration curve for this case is shown in Fig. 1.

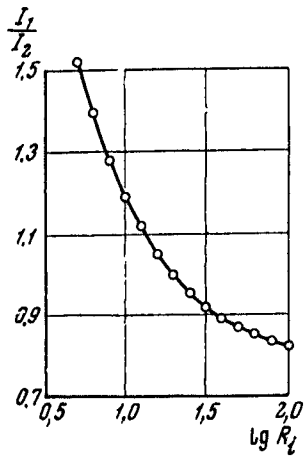

Fig. 1. Calibration curve for determining R_i by means of a slotted cell with a sectional cathode; i_1 and i_2 are the currents flowing through the first and second sections of the cathode respectively.

For checking purposes, some of the results obtained were compared with data calculated from the specific resistance of the electrolyte and the slope of the polarization curves for average current density. The two methods gave similar results on the horizontal parts of the curves corresponding to approximately linear polarization (Fig. 2). The lack of coincidence between the data is due not only to experimental error but also to the natural discrepancy existing between the average value of R_i obtained by measurement and the computed value of R_i for average current density. The average value of R_i more accurately characterizes the ability of the electrolyte to give a uniform coating on surfaces with relief.

The copper-sulfate acid electrolyte consitutes a three-component system $CuSO_4 \cdot 5H_2O$ - H_2SO_4 - H_2O and its throwing power (index R_i) may vary from a few tenths to a few tens of centimeters, depending on the composition. As a rule the most productive compositions correspond to the worst throwing powers, although there is no direct connection and in principle a high throwing power could go together with fair efficiency.

In order to prepare the electrolytes we used a concentrated solution of copper sulfate purified by sudden cooling of the supersaturated solution [11] and prolonged cathodic electrolytic purification.

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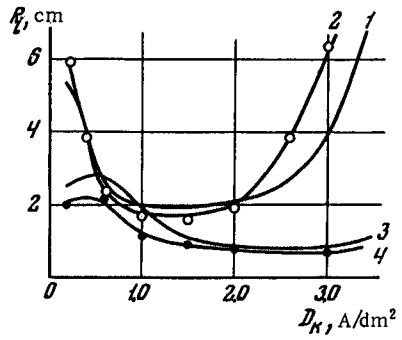

Fig. 2 Comparison between the value of R_i measured by means of the cell (2 and 4) and those calculated from the slope of the polarization curves (1 and 3). Electrolyte (g/liter) 95 $CuSO_4 \cdot 5H_2O$ and 125 H_2SO_4. 1 and 2 for 20°, 3 and 4 for 45°.

The series of solutions with the same concentration of copper sulfate contained different quantities of H_2SO_4. The value of R_i was measured at 20°, as usual for a copper-acid electrolyte. Current densities chosen for study were 1.5, 0.6, and 0.2 A/dm². The first two covered the range of current densities most frequently used in copper plating. The lowest density was interesting from the point of view of obtaining coatings similar to those given by cyanide electrolytes as regards uniformity of metal distribution.

RESULTS AND DISCUSSION

The range of concentrations used was limited by a minimum 5-g/liter concentration of H_2SO_4, since lower acid concentrations are not employed in practice, owing to side reactions involving the disproportionation of Cu^+ ions and their discharge at the cathode, leading to deterioration of the deposit [12]. The minimum content of $CuSO_4 \cdot 5H_2O$ was determined by the limiting permissible current density, and for the current densities studied varied from 25 to 90 g/liter. The maximum concentration of copper sulfate for a given concentration of acid was limited by the equilibrium curve corresponding to the limiting solubility of $CuSO_4 \cdot 5H_2O$ in H_2SO_4 solution [13]. By extrapolating the measured values (these are shown by the circles in Fig. 3a, b, c) over the concentration range studied, curves of identical R_i were plotted.

The throwing power index for all the solutions rises monotonically with falling current density and falling copper-sulfate content, reaching very high values at 50 and 25 g/liter (up to 35.5 cm). An exception is the region of small sulfuric-acid concentration (up to about 30 g/liter), where there is a slight maximum of throwing power at a copper-sulfate concentration of 150 to 200 g/liter. This is because in this range of H_2SO_4 concentrations the addition of copper sulfate leads to a very slight rise in the electrical conductivity of the solution, while the polarizability falls slightly.

It is interesting to note that the throwing-power index in an electrolyte containing, for example, 25 g/liter $CuSO_4 \cdot 5H_2O$ and 310 g/liter H_2SO_4 (R_i = 30 cm), exceeds the value of R_i for a cyanide copper-plating solution (2.41 cm) [14] and thus exceeds it in respect of the uniformity of current distribution. The possibility of obtaining very uniform desposits from acid copper-plating electrolytes has already been mentioned [8]. It should be noted, however, that the distribution of metal in a cyanide electrolyte may differ considerably from the distribution of current, owing to the variation in current efficiency with current density.

An increase in the concentration of sulfuric acid with a high $CuSO_4 \cdot 5H_2O$ content leads to a monotonic rise in R_i, the more sharply so, the lower the copper-sulfate concentration. Beginning from 100 g/liter $CuSO_4 \cdot 5H_2O$, however, a plateau appears on the R_i / acid- concentration curves, the throwing power remaining almost constant. In an electrolyte containing 25 g/liter $CuSO_4 \cdot 5H_2O$, the throwing power even falls slightly for a very large acid concentration. This nonmonotonic behavior of R_i becomes especially marked for small current densities. As may be seen from Fig. 4 (curve 2), in fact, for a current density of 0.1 A/dm² the throwing power in this electrolyte has a sharp maximum for an acid content of around 250 g/liter, which can only be explained by a change in the specific electrical conductivity (curve 3). The reason for this maximum is the change in the slope of the polarization curve with acid content in the electrolyte. Measurements in fact show (Fig. 5) that the slope of the polarization curves is greatest for an acid concentration of 200 to 300 g/liter. For a large acid concentration the polarization curves take the characteristic S shape. The polarizability for a current density of 0.1 A/dm² falls slightly with addition of acid* and this leads to a maximum of R_i at an H_2SO_4 concentration of around 250 g/liter. For a current density of 0.2 A/dm² the polarizability of all the

* One possible cause of this fall may be the dissolution of metallic copper in the presence of oxygen [12], which increases with increasing acid content, the reaction being

$$Cu + 2H^+ + {}^1/_2O_2 \rightarrow Cu^{2+} + H_2O.$$

With increasing current density this process is gradually suppressed.

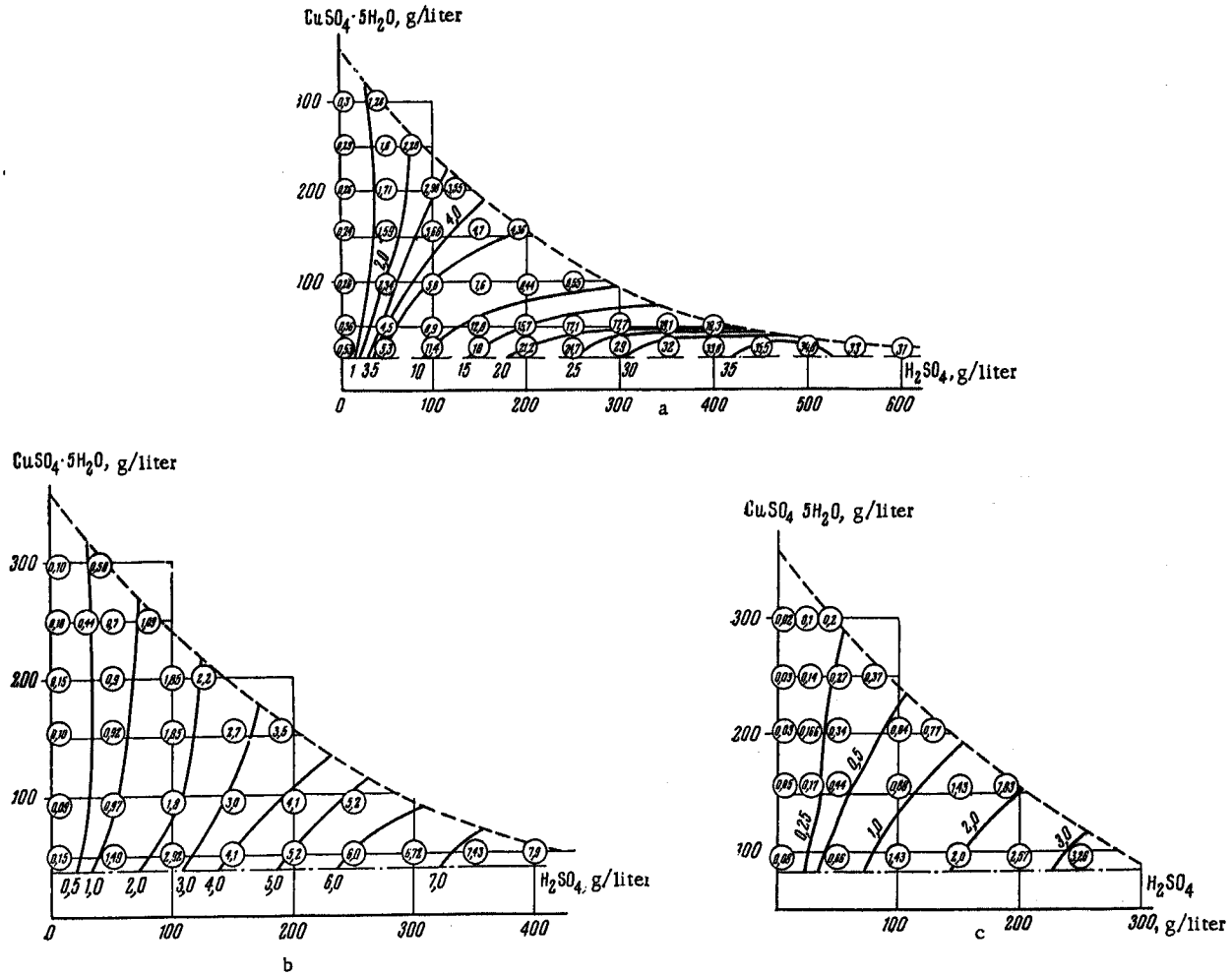

Fig. 3 Throwing-power index of copper-sulfate electrolytes as a function of composition for average current density a) 0.2, b) 0.6 c) 1.5 A/dm^2.

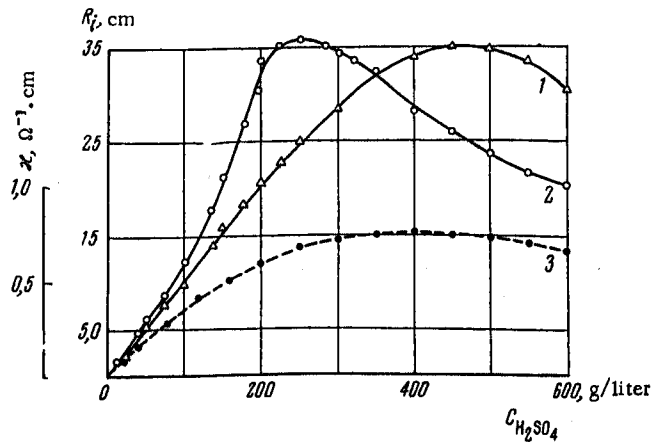

Fig. 4 Variation in the throwing-power index and specific electrical conductivity (3) of an electrolyte (25 g/liter $CuSO_4 \cdot 5H_2O$) with sulfuric-acid concentration for current density 1) 0.2, 2) 0.1 A/dm^2.

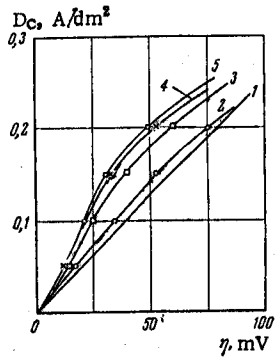

Fig. 5 Cathode polarization curves obtained in electrolytes containing 25 g/liter $CuSO_4 \cdot 5H_2O$ and various quantities of acid (g/liter): 1) 200, 2) 300, 3) 400, 4) 500, 5) 600. Temperature 25°.

solutions is approximately the same, and the change in throwing power with acidity (Fig. 4, curve 1) entirely corresponds to the change in specific electrical conductivity (Fig. 4, curve 3).

CONCLUSIONS

1. We have studied the variation of the throwing-power index in the copper-sulfate/sulfuric acid system with the concentration of the components and the current density.

2. The throwing power rises monotonically with falling current density and falling copper-sulfate concentration, reaching 35.5 cm at 25 g/liter, which exceeds the value of R_i for a cyanide copper-plating solution.

3. A rise in the sulfuric-acid concentration for a copper solphateconcentration $CuSO_4 \cdot 5H_2O > 100$ g/liter raises R_i monotonically. For lower concentrations($CuSO_4$ 50 g/liter) the dependence on acid content has a maximum, appearing more sharply at low current densities. The appearance of the maximum is due to a change in the specific electrical conductivity and a fall in polarizability with increasing acidity at low current densities.

APPENDIX. Ratio of the Currents in the Sectioned Cathode of a Slotted Bath as a Function of the Electrochemical-Similarity Criterion $E = R_i/l_0$.

E	0.01	0.0125	0.016	0.02	0.025	0.032
I_1/I_2	4.185	4.125	4.044	3.956	3.852	3.717
E	0.04	0.05	0.063	0.08	0.1	0.125
I_1/I_2	3.577	3.419	3.239	3.036	2.837	2.632
E	0.16	0.2	0.25	0.32	0.4	0.5
I_1/I_2	2.406	2.206	2.017	1.822	1.664	1.523
E	0.63	0.8	1.0	1.25	1.6	2.0
I_1/I_2	1.395	1.282	1.193	1.118	1.049	0.999
E	2.5	3.2	4.0	5.0	6.3	10
I_1/I_2	0.957	0.919	0.892	0.870	0.852	0.825

Note: $\frac{l_0}{h} = 2.8$; $l_1 = 0.438$; $l_2 = 1 - l_1$; l_0 — length of the cathode, h — distance between cathode and partition.

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